Report as of FY2010 for 2010DC115B: "Determination of Seasonal Source Variation of Hydrocarbons, Fatty Acids, Organics and Nutrients in the Anacostia River: Stable isotope Ratios of Specific Compounds"

Publications

Project 2010DC115B has resulted in no reported publications as of FY2010.

Report Follows

Determination of Seasonal Source Variation of Hydrocarbons, Organics and Nutrients in the Anacostia River: Stable Isotope Ratios of Specific Compounds

Progress Report

Submitted to

DISTRICT OF COLUMBIA WATER RESOURCES RESEARCH INSTITUTE

By

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Progress Summary

A six month no-cost extension was granted March 3, 2011 so the final report of the project will be delivered by October 31, 2011. Water, sediment, and (when possible) invertebrate samples have been collected (in most cases monthly) since April 2010 and have continued through May 2011. We have completed $d^{13}C$ and $d^{15}N$ on organics (sediment and water column particulate organic matter (POM)) from the first 9 months or so of the collections. Hydrocarbons have been extracted from those same samples and have been characterized with the GC/MS. Also, characterization of the geochemistry of Anacostia waters from our field sites has been and continues to be undertaken (analysis of inorganics, including Ca, Mg, Na, S, K, P, B, Ba, Ni, Co, plus nutrients, including NO_3, NH_4, PO_4, and total organic carbon (TOC). The examination and interpretation of our results is ongoing, however I have included in the progress report our initial analysis, which has been presented at the Annual Meeting of the American Geophysical Union, December 2010. These results will be written up as a manuscript for peer reviewed publication summer 2011. We have yet to decide which of our hydrocarbon extracts should be selected for $d^{13}C$ characterization. Generally, only samples with compounds of particular interest (branched or odd chain fatty acids, or petrochemicals for example) should be selected because compound specific isotope analysis is a complex and expensive procedure. We have to send our sediment and POM samples out for $d^{34}S$ analysis. Due to expense, we had to delay this analysis until the funding for the project was in place. We expect to have all the data collected by early fall, and will review what we find in the final report.

Below please find our initial analysis of our results from the geochemical/nutrient work.

Seasonal nutrient dynamics in the Anacostia River (D.C., USA): geochemistry and hydrocarbon biomarkers*

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* This paper was presented at the Annual Meeting of the American Geophysical Union, San Francisco, December 2010 B43A-0446 poster session

Abstract

The seasonal biogeochemistry of the urban Anacostia River (Washington D.C. USA) was investigated. Chemical parameters examined include: inorganics (Ca, Mg, Na, S, K, P, NO3, NH4, PO4, B, Ba, Ni, Co); fatty acids and other hydrocarbons; C, N and S stable isotopes; and other water chemistry indicators (hardness, salinity, alkalinity, soluble salts, SAR, TDS). Between April and September 2010, water and sediment were sampled from three tidal freshwater sites along the Anacostia River (UP, MID, and DOWN). Stable isotope analysis of surface sediments revealed a lack of temporal variation in the sources of carbon and nitrogen to the Anacostia. δ15N values ranged from +2 to +6‰, with the most enriched sediment occurring at DOWN (+4 to +6‰). While these values do not reflect sewage inputs, an overall enrichment is observed between spring and late summer, which may indicate microbial activity. δ13C values exhibited slightly more variation and ranged from -30 to -25‰. All sites showed relative depletion in early summer compared with spring or late summer/fall. Water nutrients (NO3 and NH4) demonstrate seasonal fluxes; all sites show a peak in nutrients during early summer (June) and subsequent decline. Overall, NO3 ranges from about 0.2 to 3.3 mg/L and NH4 ranges from 0 to 1.7 µg/L. Preliminary GC-MS analysis of isolated fatty acids does not explicitly suggest bacterial or higher plant dominance in the spring; however, some notable compounds were identified, such as the PAH fluoranthene, naphthoquinone, and testosterone, as well as a number of cholesterols and other steroids. Principle Component Analysis (PCA) of the chemistry data suggests mineral geochemical variables, rather than inorganic nutrients, are the driving forces of observed trends.

Introduction

The Anacostia River is a major waterway, encompassing 440 km^2, located in Washington, D.C. It is also one of the nation's 10 most contaminated rivers, containing sewage, metals, PAHs, and PCBs, and has been cited by the EPA as a "major area of concern" for the Chesapeake region (Maa 2008). Several studies have examined heavy metal geochemistry in the river, but its biogeochemical processes remain largely unstudied (MacAvoy *et al*. 2009). This paper examines nutrient dynamics, organic material sources, and microorganism community makeup, as well as the seasonal trends in these parameters.

Objectives

This research seeks to elucidate seasonal nutrient dynamics and organic material sources of the Anacostia River by addressing the objectives: 1) Determine if seasonal component to water nutrient concentrations and sources exists, and 2) Identify biogeochemical controls within the river and discern which geochemical and nutrient variables are driving those controls.

Methods

Sampling was conducted at three sites (UP, MID, DOWN) along a downstream gradient originating in Bladensburg, Maryland (Plate 2). Water column and sediment samples were collected in triplicate from each site on a once monthly basis, starting in April, 2010. Water samples were immediately filtered onto GFF once in lab, while replicates were sent to Cornell's Nutrient Analysis Lab for analysis of inorganics (Ca, Mg, Na, S, K, P, NO3, NH4, PO4, B, Ba, Ni, Co). Sediment samples were dried for 72 hours at 60°C.

Extracted sediment samples and water column particulate organic matter (POM) were sent to UC Davis' Isotope Analysis Facility for ^{13}C and ^{15}N isotope analyses using a PDZ Europa ANCA-GSL elemental analyzer interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer. Fatty acids were extracted from GFFs and sediment via Soxhlet extraction followed by saponification. FAMEs were analyzed using a Thermo Polaris Q GC/MS. A Principle Components Analysis (PCA) was applied to nutrient variables to elucidate relationships of covariance within the dataset (Dennis *et al.*, 1995).

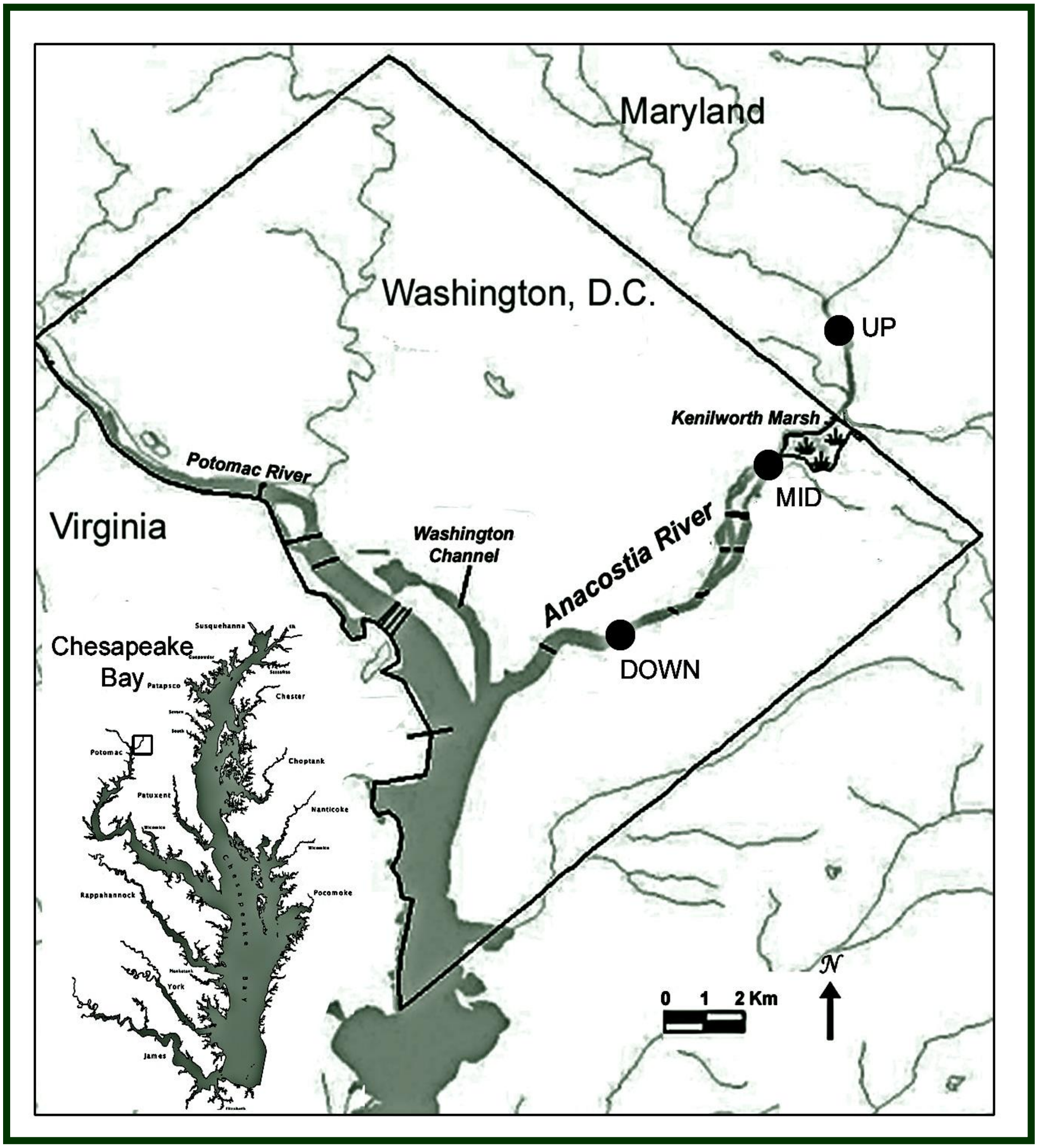
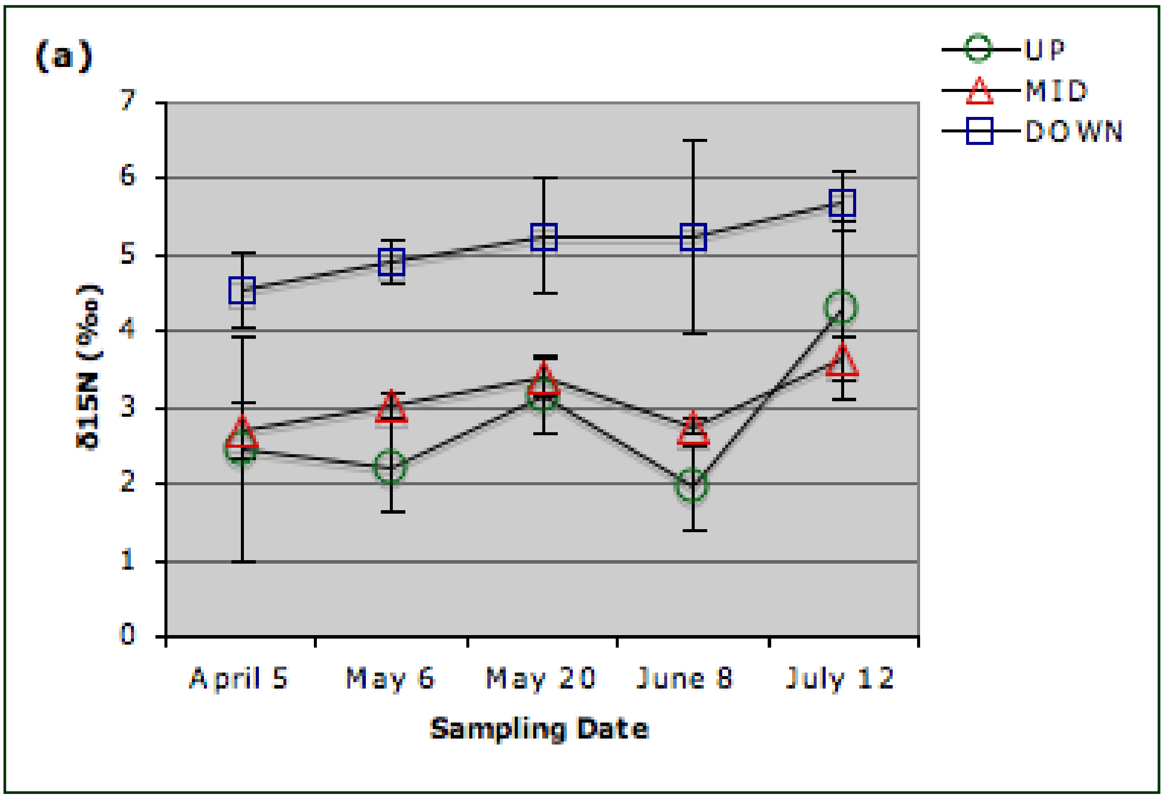


Plate 1. Site map.

Figure 1 Sediment Nitrogen (a) and Carbon (b) Isotope Values over Time: (a) δ15N values are observed to increase from April to July at all sites. Sediment at DOWN shows the most enriched isotope signature, which could reflect its proximity to a combined sewage outflow. Overall, sediment is less enriched than would be expected if sewage is a source; N source appears to be autochthonous (b) δ13C shows similar trends at all sites, and becomes more enriched from ate May to September. Values range from -25‰ to -30‰, and are not reflective of a terrestrial source.



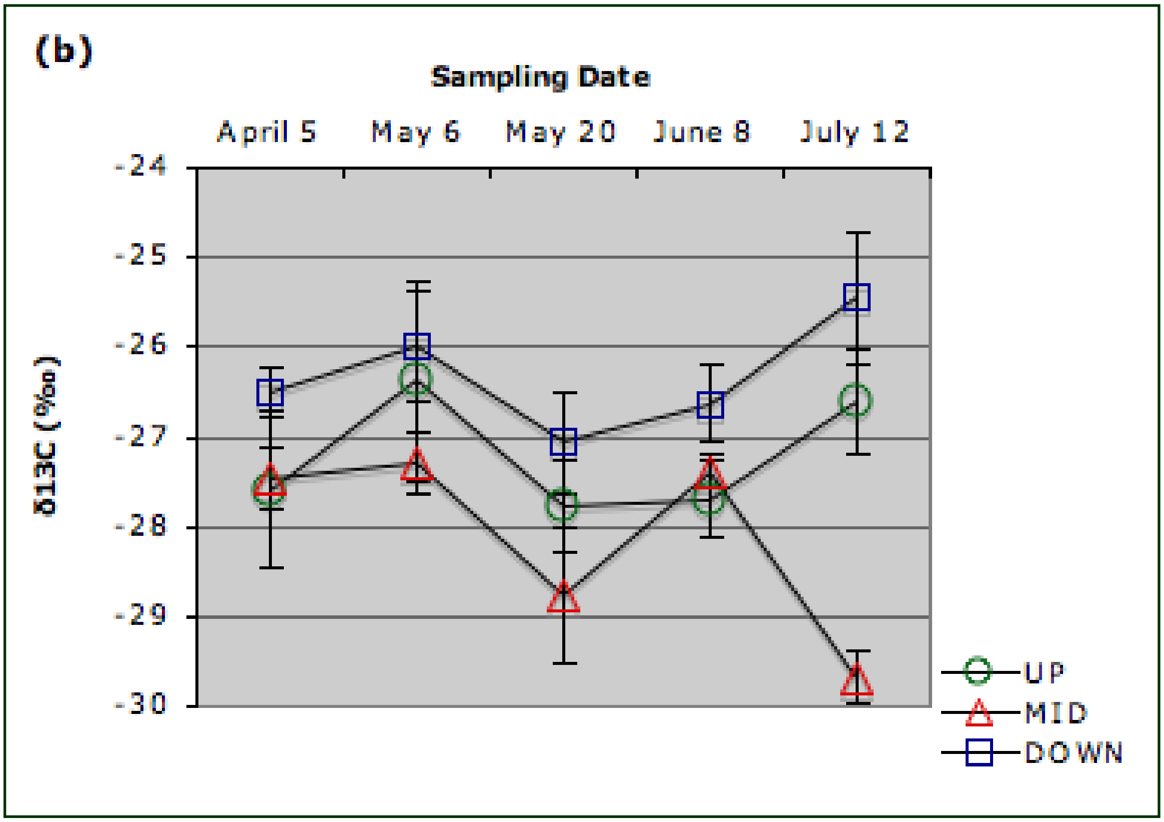
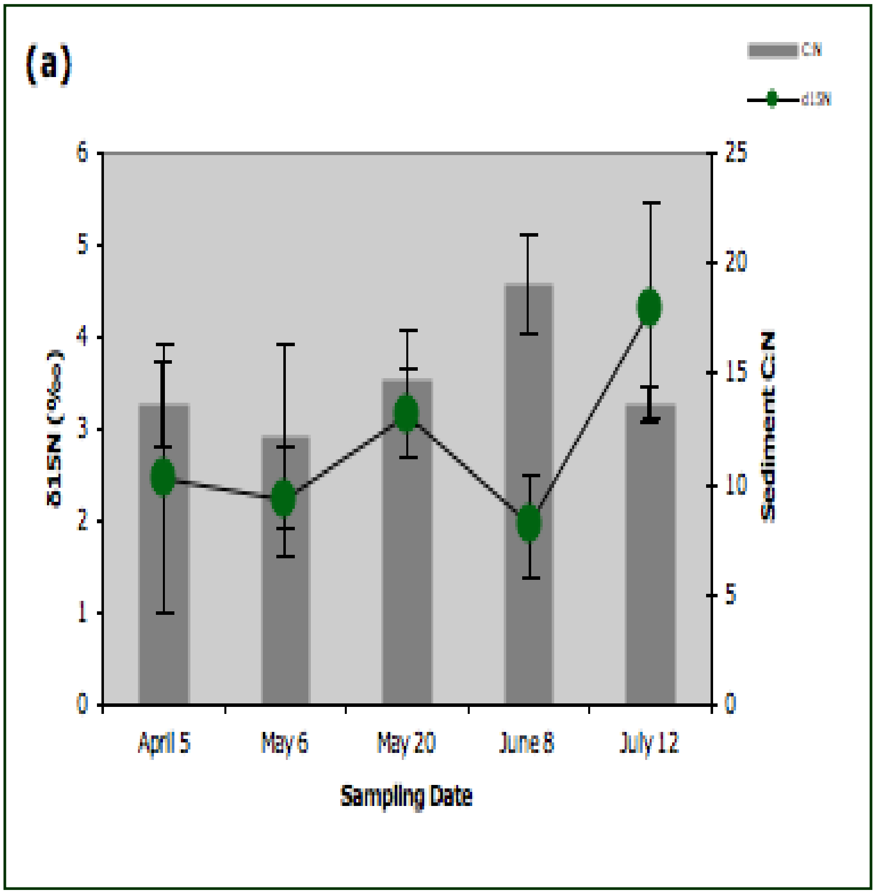
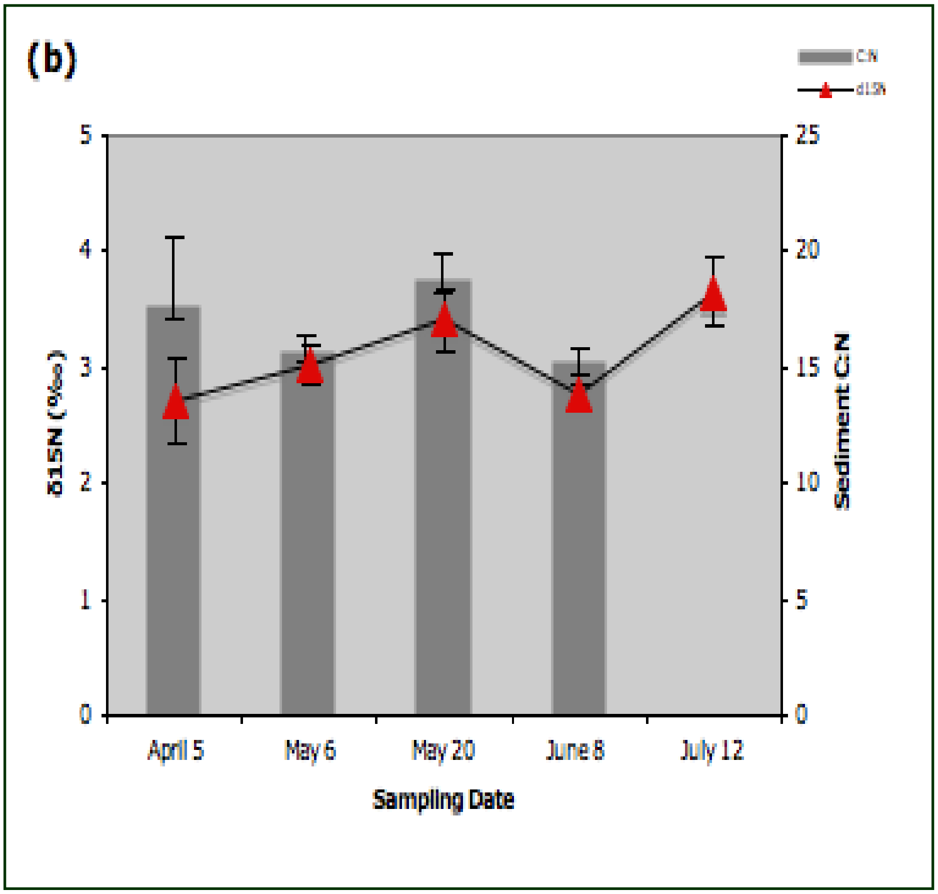

(b)
Sampling Date
April 5
May 6
May 20
June 8
July 12
δ13C (‰)
-24
-25
-26
-27
-28
-29
-30
UP
MID
DOWN

Figure 2 Sediment δ15N and C:N over Time at (a) UP, (b) MID, and (c) DOWN: (a,b,c) C:N is relatively constant over time at all sites, ranging from about 14 to 20. At all sites, sediment nitrogen is becoming more enriched between spring and late summer, reflective of increased in microbial activity. (c) DOWN shows the most nitrogen enrichment, with δ15N values range from +4 to +6‰.




(b)
C:N
d15N
δ15N (‰)
Sediment C:N
0
1
2
3
4
5
0
5
10
15
20
25
April 5
May 6
May 20
June 8
July 12
Sampling Date

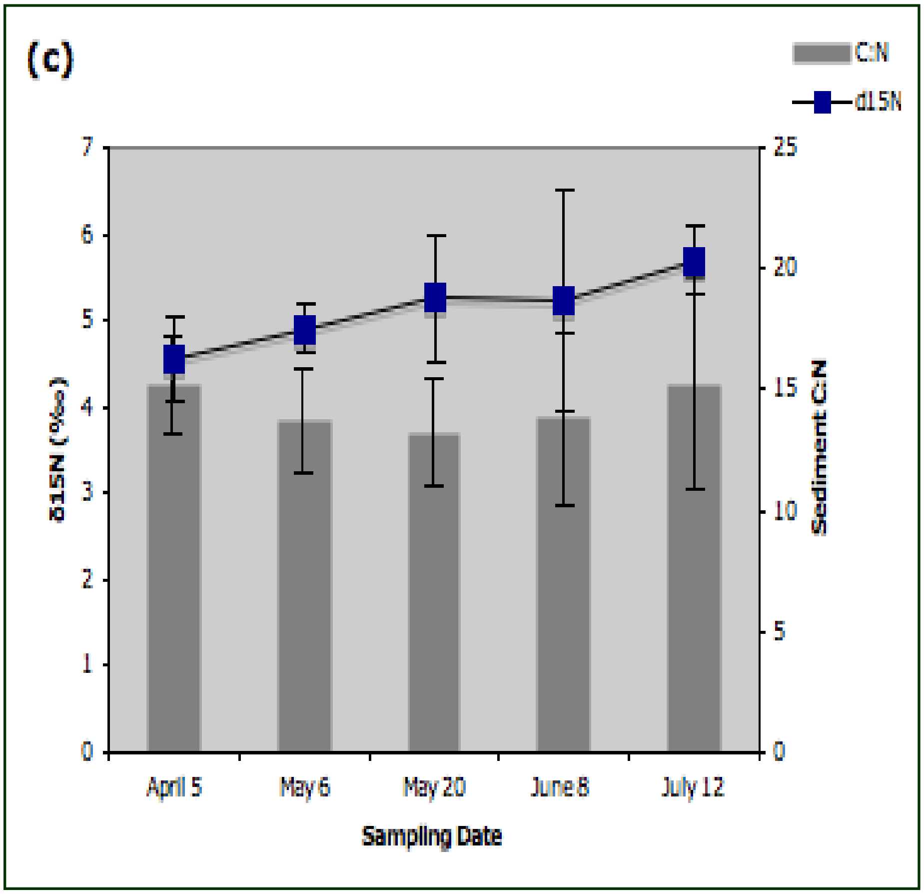
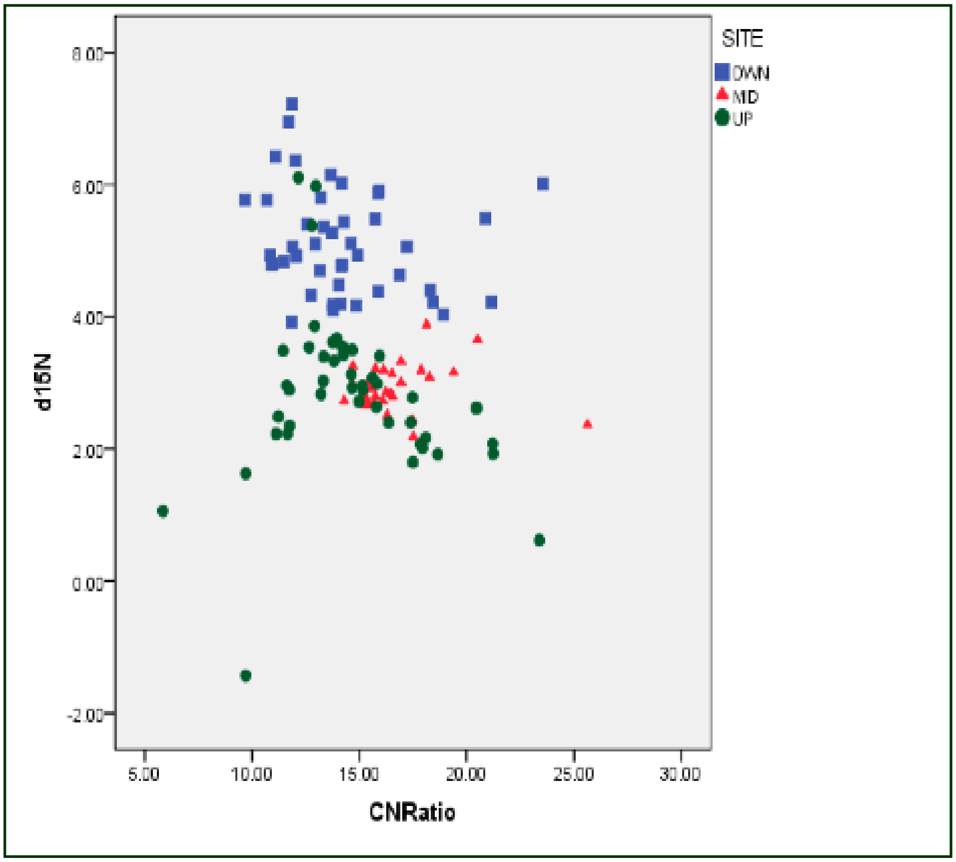
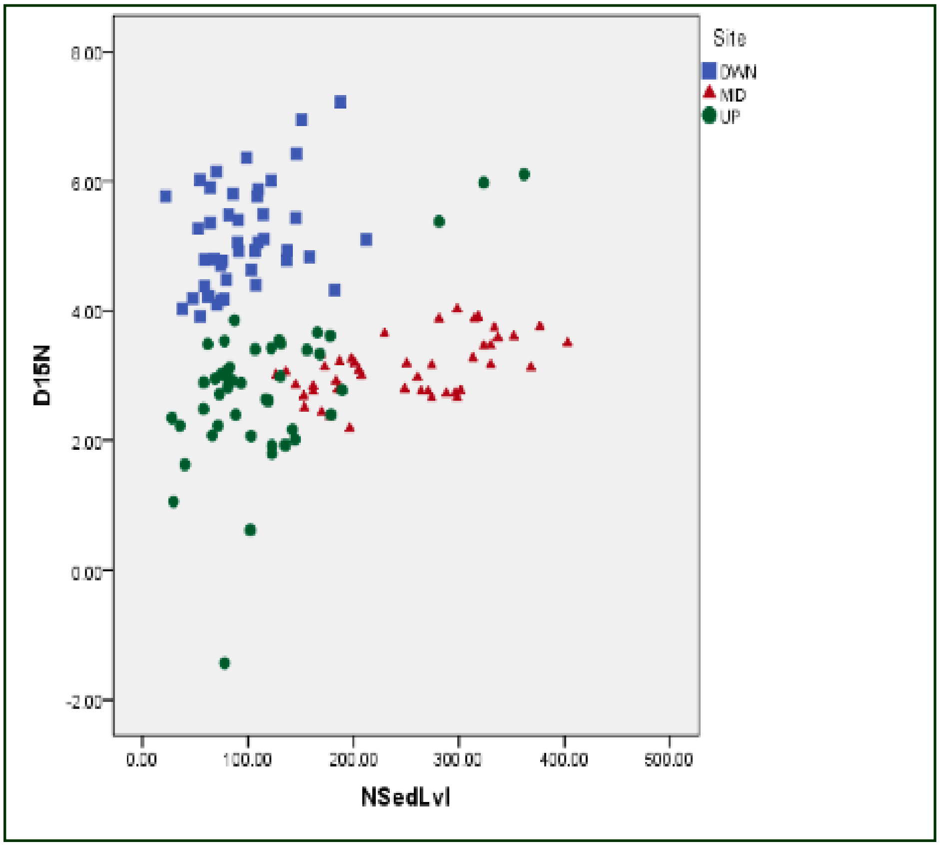

(c)
C:N
d15N
δ15N (‰)
Sediment C:N
April 5
May 6
May 20
June 8
July 12
Sampling Date
0
1
2
3
4
5
6
7
0
5
10
15
20
25

Figure 3 δ15N versus C:N (a) and Soil [N] (b) shows Clustering by Site: clustering in figures 3 (a) and (b) suggests that sediment [C] is highly variable between sites UP and DOWN.

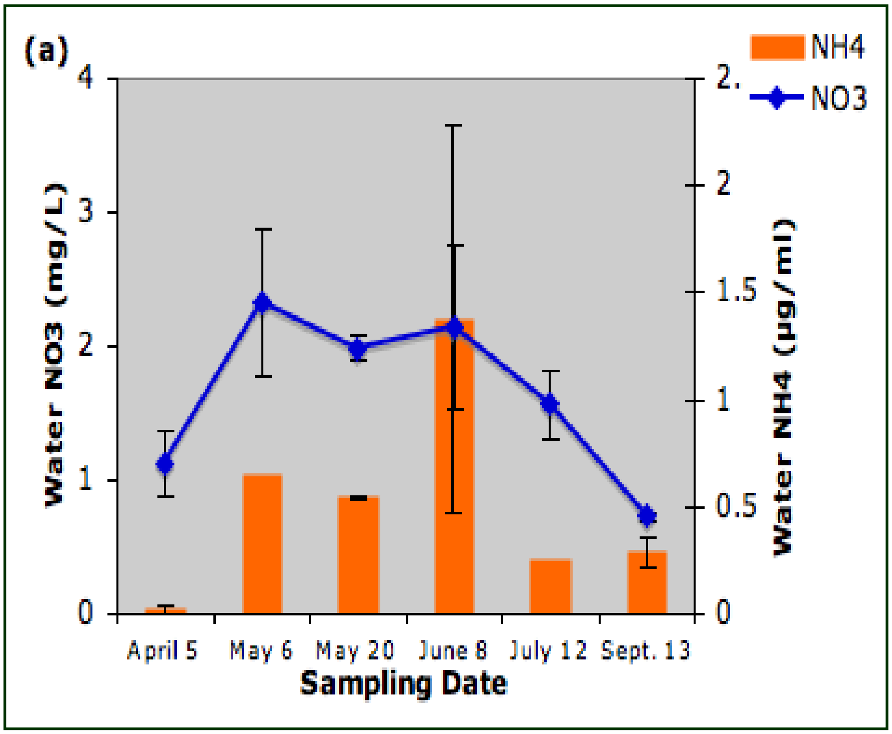


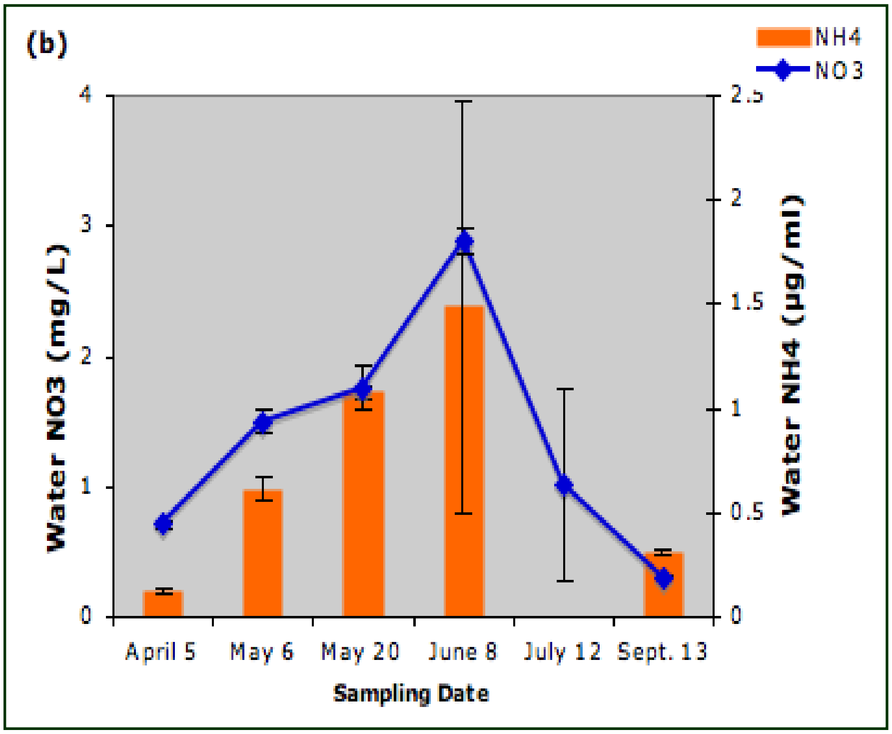
3a.


Site
DWN
MD
UP
8.00
6.00
4.00
2.00
0.00
-2.00
D15N
0.00
100.00
200.00
300.00
400.00
500.00
NSedLvl

3b.

Figure 4 Water Column Nitrogen (NO3 and NOH4) Trends over Time: At (a) UP, (b) MID, and (c) DOWN. Nutrient levels are within similar ranges at all sites and are variable across the time span of sampling. (b) a gradual increase in both parameters is exhibited at MID, with a peak in June and subsequent decline. (c) a pulse of NO3 is seen in May, uncouple with any NH4 increase.




(b)
NH4
NO3
Water NO3 (mg/L)
Water NH4 (µg/ml)
April 5
May 6
May 20
June 8
July 12
Sept. 13
Sampling Date

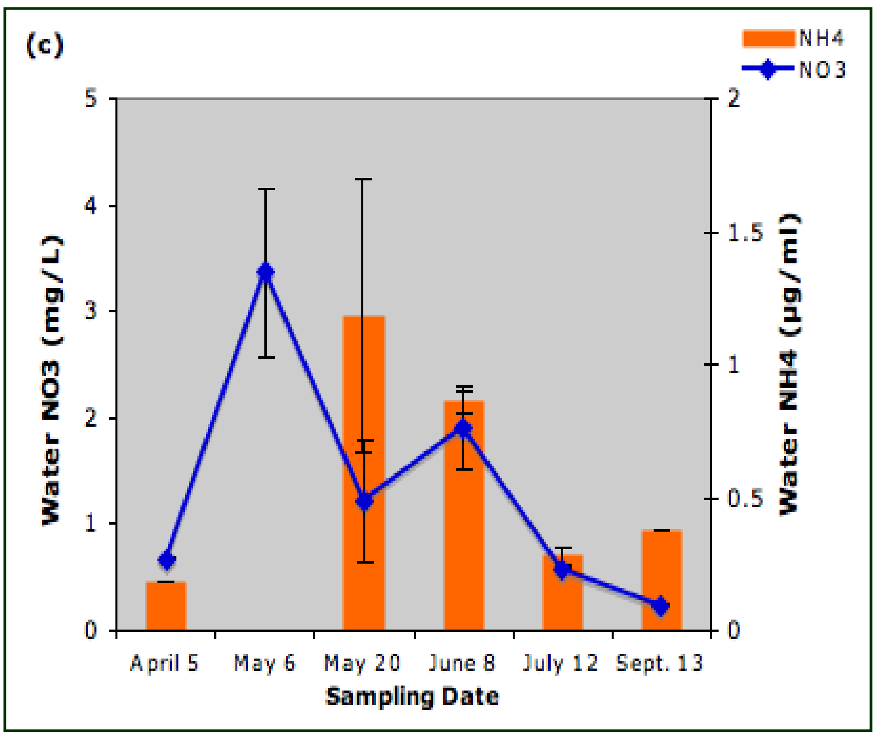
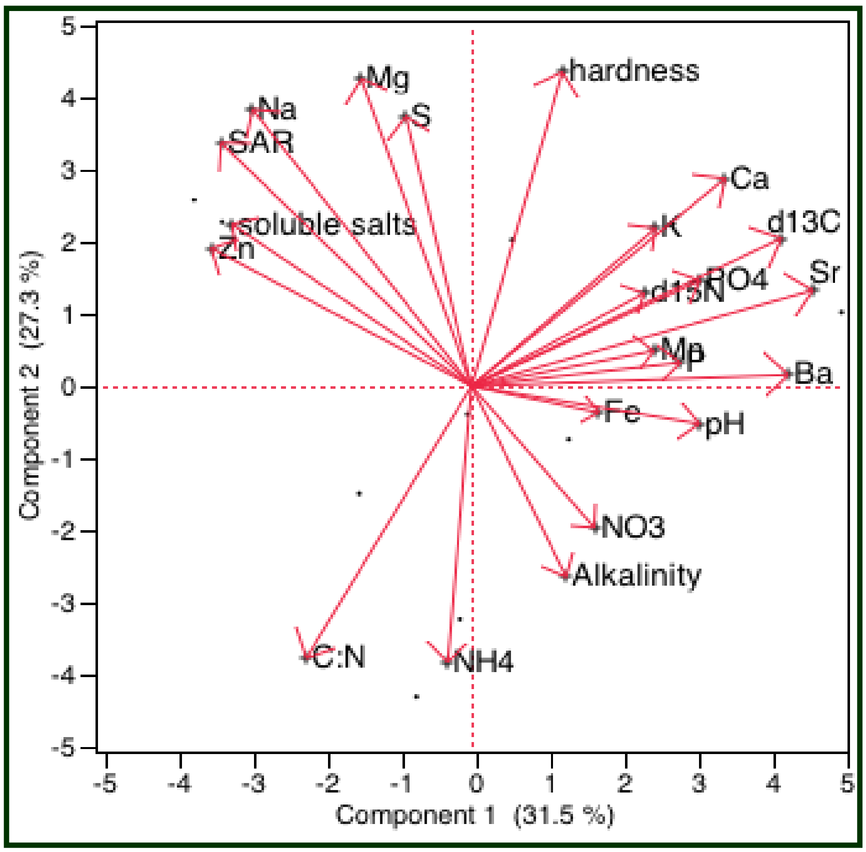
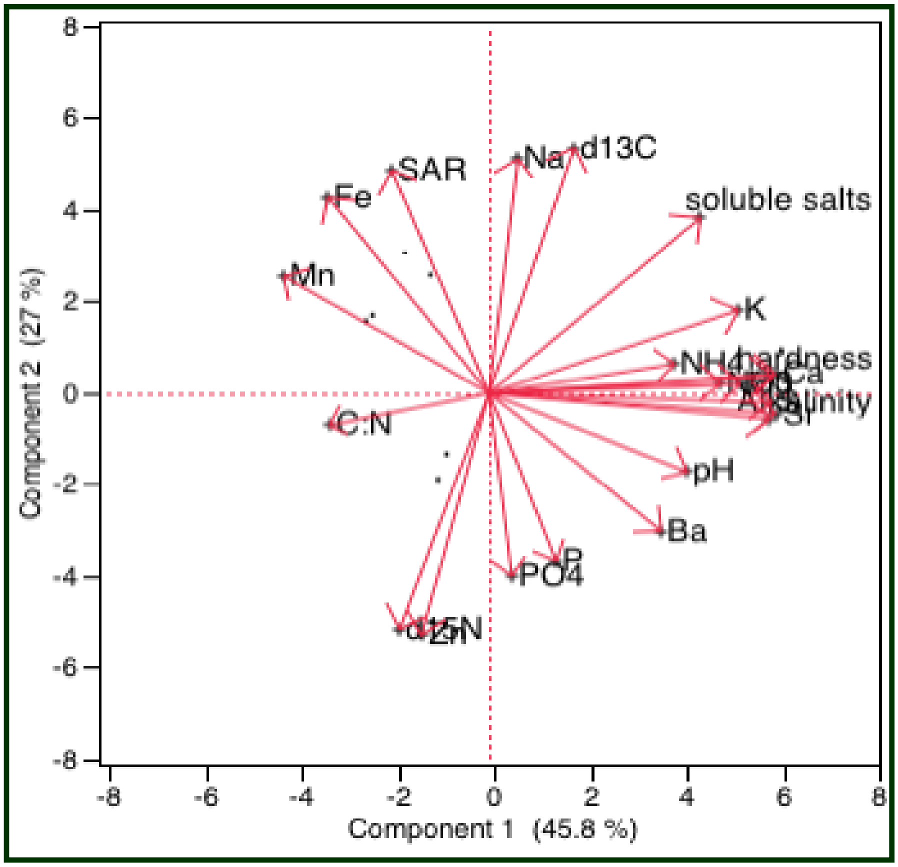

(c)
NH4
NO3
Water NO3 (mg/L)
Water NH4 (µg/ml)
April 5
May 6
May 20
June 8
July 12
Sept. 13
Sampling Date

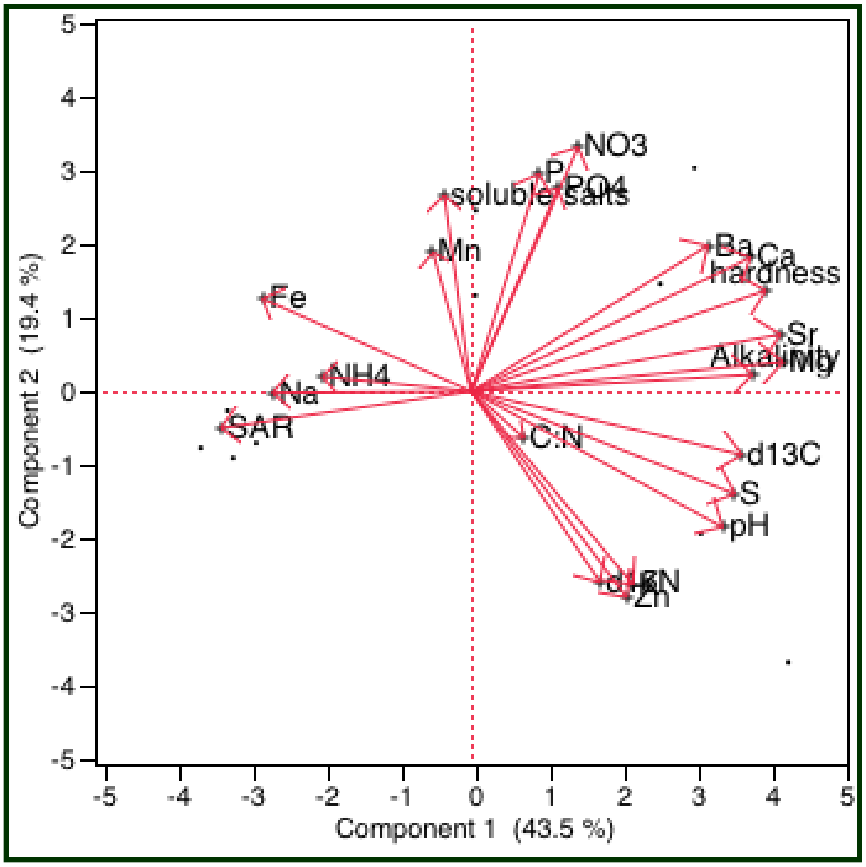
Figure 5 Biplots of PCA at UP (a), MID (b), and DOWN (c): PCA including all water and sediment parameters reveals that each site has distinct controls. There appears to be a strong geochemical control to explain most of the dataset (PC1), while PC2 highlights nutrient drivers such as δ15N and C:N. (b, c) there is a strong correlation between Zn levels and δ15N at both sites MID and DOWN. (a, c) at UP and DOWN δ13C is strongly associated with geochemical variables.



5a.


Component 2 (27 %)
Component 1 (45.8 %)
8
6
4
2
0
-2
-4
-6
-8
-8
-6
-4
-2
0
2
4
6
8
SAR
Fe
Mn
Na
d13C
soluble salts
K
NH4
hardness
Ca
alkalinity
Sr
C:N
pH
Ba
P
PO4
d15N
Zn

5b.



5c.

Conclusions

1) A seasonal component is present in water nutrient concentrations; however variation is sediment organic sources (δ15N, δ13C, C:N) appears more closely associated with site rather than collection date.

2) δ13C (-25 to -30‰) are representative of autochthonous production.

3) δ15N values ranged (+2 to +6), but UP showed the most enrichment (+4 to +6). Values are not reflective of sewage inputs. δ15N values also show a gradual enrichment from April to July, which may suggest the increase is bacterial mobilization.

4) C:N ratios of between 13 and 19 suggest autochthonous sources of sediment organics.

5) Heterogeneity between sites values is highlighted in Figure 1(a) and Figure 4. PCA reveals strong geochemical (mineral) involvement in PC1 and more nutrient involvement in PC2. Each site is seen to have distinct biogeochemical controls (Figure 5).

Acknowledgments

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References

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